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(54) 【発明の名称】 非水電解質二次電池

(57) 【要約】

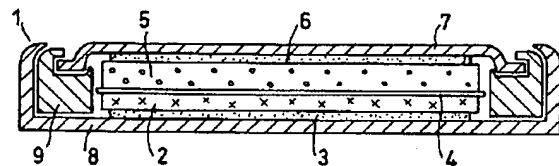
【課題】 本発明は、室温を超える温度で充放電を繰り返した場合でも充放電容量の低下の少ない非水電解質二次電池を提供するものである。

【解決手段】 本発明は、正極材料として、前記正極材料の立方晶  $Fd3m$  で帰属した格子定数  $a_0$  (オングストローム) と指数 (400) と (311) の回折線の強さを表す  $I(400)$  と  $I(311)$  の比  $R = I(400) / I(311)$  を下記 (式1)

$$\beta = 537.6 \times (a_0 - 8.398) \times (R^2 - 2.1616 \times R + 1.0955)$$

(式1)

に代入した  $\beta$  の値が  $\beta \geq 6$  であるリチウムマンガ酸化物を用いたものである。



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# PATENT ABSTRACTS OF JAPAN

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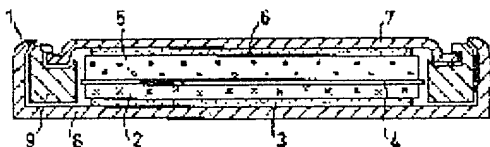
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## (54) NONAQUEOUS ELECTROLYTE SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a nonaqueous electrolyte secondary battery which exhibits only a small decrease in the charge/discharge capacity even when charge/discharge is repeated at a temperature above the room temperature.

SOLUTION: A positive electrode material layer 2 is constructed by a mixed body such as a positive electrode material, a conductive agent and a binding agent, for example. Lithium manganese oxide is used as the positive electrode material, whose lattice constant  $aO$  (angstrom) belonging to the cubic  $Fd3m$  system of the positive electrode material and a ratio  $R=I(400)/I(311)$  showed an intensity of a diffraction line of exponents (400) and (311) are substituted in a formula 1:  $\beta=537.6 \times (aO-8.398) \times (R^2-2.1616 \times R+1.0955)$ , and value of  $\beta$  should be established  $\beta \geq$ .



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## CLAIMS

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[Claim(s)]

[Claim 1] In the nonaqueous electrolyte rechargeable battery possessing the positive electrode which contains a lithium manganic acid ghost as a positive-electrode ingredient, a separator and the electrode group which consists of a negative electrode, and nonaqueous electrolyte said positive-electrode ingredient It is the following (formula 1) about intensity ratio  $R = I(400) / [I(400) + I(311)]$  showing the lattice constant  $a_0$  (angstrom), the characteristic (400), and the diffraction line intensity of (311) which belonged by cubic  $Fd\bar{3}m$  of said positive-electrode ingredient.  
 $\beta = 537.6 \times (a_0 - 8.398) \times (R^2 - 2.1616 \times R + 1.0955)$  (formula 1) Nonaqueous electrolyte rechargeable battery characterized by the value of substituted  $\beta$  being  $\beta \geq 6$ .

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the nonaqueous electrolyte rechargeable battery which improved the positive-electrode ingredient.

[0002]

[Description of the Prior Art] In recent years, researches and developments of the rechargeable lithium-ion battery which is a nonaqueous electrolyte rechargeable battery as the power source are actively done with development of the information terminal of the remarkable pocket mold of spread. As a positive-electrode ingredient of such a nonaqueous electrolyte rechargeable battery,  $\text{LiCo}_2\text{O}_4$  has mainly been used. However, since Co of a raw material is expensive and there are also few underground reserves, researches and developments of the lithium manganic acid ghost ( $\text{LiMn}_2\text{O}_4$ ) which used cheap Mn also with abundant underground reserves for the raw material as an ingredient which replaces this are done briskly.

[0003] However, the nonaqueous electrolyte rechargeable battery which used the conventional lithium manganic acid ghost for the positive-electrode ingredient had the problem (cycle capacity fall) to which capacity falls quickly, when the cycle of charge and discharge was repeated, and especially at the temperature exceeding the room temperature which is a practical temperature requirement, with a temperature rise, the cycle capacity fall was remarkable and did not spread widely until now.

[0004]

[Problem(s) to be Solved by the Invention] Then, this invention aims at a cycle capacity fall offering the practical nonaqueous electrolyte rechargeable battery using few lithium manganic acid ghosts as a positive-electrode ingredient also at the temperature exceeding a room temperature.

[0005]

[Means for Solving the Problem] In the nonaqueous electrolyte rechargeable battery

possessing the electrode group which this invention becomes from the positive electrode which contains a lithium manganic acid ghost as a positive-electrode ingredient, a separator, and a negative electrode in order to solve the above-mentioned technical problem, and nonaqueous electrolyte Said positive-electrode ingredient is the following (formula 1) about intensity ratio  $R=I(400)/[I(400)+I(311)]$  showing the lattice constant  $a_0$  (angstrom), the characteristic (400), and the diffraction line intensity of (311) which belonged by cubic  $Fd3m$  of said positive-electrode ingredient.

$\beta = 537.6 \times (a_0 - 8.398) \times (R^2 - 2.1616 \times R + 1.0955)$  (formula 1)

It is the nonaqueous electrolyte rechargeable battery characterized by the value of  $\beta$  boiled and substituted being  $\beta \geq 6$ .

[0006] According to research of this invention persons, the cause of the cycle capacity fall under high temperature mainly originates in the instability of the manganese atom in the crystal structure of the lithium manganic acid ghost of a positive electrode, and in order to move from the location in the crystal structure which should have a manganese atom essentially in connection with the insertion desorption of the lithium ion accompanying charge and discharge, it is presumed that a crystal structure is destroyed gradually.

[0007] Then, in this invention, in order to raise the stability of the manganese atom in the crystal structure and to improve cycle capacity degradation under high temperature, the lithium manganic acid ghost which fulfills specific conditions with intensity ratio  $R=I(400)/[I(400)+I(311)]$  showing a lattice constant, a characteristic (400), and the diffraction line intensity of (311) is used.

[0008] Mainly depending on the distance between oxygen atoms from which a lattice constant serves as a frame of the crystal structure of a lithium manganic acid ghost, if the distance between oxygen atoms becomes small, a lattice constant will also become small. And since the connection of a manganese atom and an oxygen atom located in the center of the regular octahedron which an oxygen atom forms will become stronger if the distance between oxygen atoms is contracted, the cycle capacity fall in an elevated temperature is improved as the increase of stability, and its result. However, it is not desirable in order to check lithium ion insertion desorption conversely and to cause the fall of capacity shortly, if spacing of an oxygen atom becomes narrow too much, namely, a lattice constant becomes small too much. then -- although a certain optimum value exists in spacing of an oxygen atom, i.e., a lattice constant, -- the optimum value -- said intensity ratio  $R$  -- close -- related -- an experiment of this invention persons -- being based (formula 1) -- it became clear that it is the case where the value of  $\beta$  shown is set to  $\beta \geq 6$ .

[0009] Moreover, mainly depending on the location where the lithium atom in the crystal structure of a lithium manganic acid ghost and a manganese atom occupy an intensity ratio  $R$ , a lithium atom and a manganese atom occupy 8a site and 16d site ideally in the lithium manganic acid ghost shown by cubic  $Fd3m$ , respectively. However, some of lithium atoms and manganese atoms exchange the location easily in process of composition, and this is reducing the stability of a manganese atom. Exchange of the site of the lithium atom described here and a manganese atom is strongly reflected to an intensity ratio  $R$ , and if exchange of the site of a lithium atom and a manganese atom takes place, this intensity ratio will become small. Therefore, the large thing of an intensity ratio  $R$  is desirable. However, since the intensity ratio of an X diffraction does

not necessarily reflect in coincidence only the location which a lithium atom and a manganese atom occupy reflecting some factors of a crystal structure, when an intensity ratio  $R$  becomes large too much, it will show turbulence of crystal structures other than the location of a lithium atom and a manganese atom on the contrary, and will cause a capacity fall. the optimum value of the intensity ratio  $R$  -- above -- a lattice constant -- close -- related -- an experiment of this invention persons -- being based (formula 1) -- it became clear that it is the case where the value of  $\beta$  shown is set to  $\beta \geq 6$ .

[0010]

[Embodiment of the Invention] The nonaqueous electrolyte rechargeable battery (for example, carbon button mold nonaqueous electrolyte rechargeable battery) in connection with this invention is explained to a detail with reference to drawing 1.

[0011] For example, the nonaqueous electrolyte rechargeable battery 1 consists of the positive electrode which consists of a positive-electrode ingredient layer 2 and a positive-electrode charge collector 3, a separator 4, the negative electrode which consists of a negative-electrode ingredient layer 5 and a negative-electrode charge collector 6, the cell lid 7 and the cell can 8, and a gasket 9, and contains the electrolytic solution inside further. The positive-electrode ingredient layer 2 consists of a mixture of for example, a positive-electrode ingredient, and an electric conduction agent and a binder, and is stuck to the positive-electrode charge collector 3 by pressure. The positive-electrode charge collector 3 is a vesicular structure object made from stainless steel, and is welded to the cell can 8. The negative-electrode ingredient layer 5 consists for example, of a lithium metal, and is stuck to the negative-electrode charge collector 6 by pressure. The negative-electrode charge collector 6 is a vesicular structure object made from nickel, and is stuck to the cell lid 7 by pressure. The positive-electrode ingredient layer 2 and the negative-electrode ingredient layer 5 have countered through the separator 4 containing the electrolytic solution. For example, the cell lid 7 and the cell can 8 which consist of stainless steel serve both as the negative-electrode terminal and the positive-electrode terminal, respectively. And it obturates the cell lid 7 and the cell can 8 in total in the gasket 9.

[0012] However, the configuration of the nonaqueous electrolyte cell concerning this invention may not be limited to the above-mentioned configuration, and may be a configuration besides a carbon button mold as occasion demands [, such as a square shape, cylindrical, and a sheet metal mold, ].

[0013] Next, the positive electrode concerning this invention, a separator, a negative electrode, and nonaqueous electrolyte are explained in detail.

(Positive electrode) Especially the nonaqueous electrolyte rechargeable battery of this invention uses the specific lithium manganic acid ghost whose value of  $\beta$  when the ratio showing the lattice constant  $a_0$  (angstrom) which belonged by cubic  $Fd3m$  as a positive-electrode ingredient, a characteristic (400), and the diffraction line intensity of (311) of  $I(400)$  and  $I(311)$  is substituted for (a formula 1) is  $\beta \geq 6$ .

[0014] In this invention, it is desirable still more desirable that it is  $12 \geq \beta \geq 6$ , and the value of  $\beta$  shown by the above-mentioned formula (1) is  $10 \geq \beta \geq 7$ . A cycle capacity fall progresses at the temperature which exceeds a room temperature as the value of  $\beta$  is less than six, and when the value of  $\beta$  is too large, there is fear of a discharge capacity fall.

[0015] The lithium manganic acid ghost concerning this invention has Spinel structure.

Empirical formula  $\text{Li}_{1+x}\text{MyMn}_{2-x-y}\text{O}_4$  (O, A) (However, M expresses one or more kinds of elements other than Mn which can serve as a tetravalent cation from univalent, and A expresses elements other than the oxygen which can serve as an anion with which  $\text{O}^{2-}$  differs from a valence, and x and y express a presentation ratio.) It is desirable for the improvement in capacity, and fall prevention of cycle capacity that it is the lithium manganic acid ghost expressed.

[0016] In the above-mentioned empirical formula, as for Element M, magnesium, aluminum, chromium, iron, nickel, cobalt, Lithium, sulfur, copper, etc. are mentioned. Since toxicity is low and especially magnesium, aluminum, cobalt, and iron have it, they are desirable. [ cheap ]

[0017] Moreover, as for Element A, it is desirable that they are a fluorine and nitrogen, and since the rate property of a fluorine [ especially ] of a cell improves, it is desirable. As for the amount of permutations of Element A, it is desirable for atomic ratio A/O of Element A and Oxygen O to be 0.1 (for 0 to be included) or less.

[0018] Moreover, as for x, it is [ 0.1 or less / -0.05 or more / and Y ] desirable that it is or more 0.25 or less range because of the improvement in capacity, and fall prevention of cycle capacity.

[0019] Moreover, generally, like the large-sized cell carried in an electric vehicle etc., when a high current is passed and charge-and-discharge capacity with them is required, the thing with a big specific surface area of a positive-electrode ingredient is made advantageous. [ there are few voltage drops and sufficient ] The reason is so easy [ migration / migration of the lithium ion between the positive-electrode ingredients and electrolytes in charge and discharge enlarges specific surface area of a positive-electrode ingredient, and ] that a touch area with the electrolytic solution is large. However, it was difficult for a positive-electrode ingredient and an electrolyte to react in an elevated temperature, and to form an inactive layer, if specific surface area is enlarged, to result in bringing the fall of a hot cycle capacity forward, and to reconcile a hot cycle-life property and a hot high current discharge property.

[0020] However, if the lithium manganic acid ghost concerning this invention is used, it is possible to enlarge specific surface area and to attain improvement in a hot cycle-life property and a high current property to coincidence by not being concerned with specific surface area, since there are few falls of a hot cycle capacity.

(Composition of a positive-electrode ingredient) A common lithium compound, for example, a lithium carbonate, a lithium hydroxide, and a lithium nitrate can be used for the lithium raw material for compounding the lithium manganic acid ghost concerning this invention. Especially, a reactant high lithium hydroxide with a manganese raw material and a lithium nitrate are desirable at the low melting point. Moreover, a manganese compound also with a common manganese raw material can be used, for example, manganese carbonate, a manganese dioxide, manganese nitrate, manganese acetate, etc. can be used.

[0021] A synthetic approach is also good by the general synthetic approach. For example, although a solid-state-solid-state reaction, a sinking-in melt method, spray dry, a spraying pyrolysis, freeze-dry, hydrothermal synthesis, etc. are mentioned, it is not limited to especially these approaches.

[0022] It is necessary to fill with this invention the certain conditions which exist when the ratio showing the lattice constant  $a_0$  (angstrom) which belonged by cubic  $\text{Fd}\overline{3}\text{m}$ , a

characteristic (400), and the diffraction line intensity of (311) of I (400) and I (311) is substituted for a formula 1. For that purpose, although it is necessary to control the intensity ratio of a lattice constant and a diffraction line, the control approach is described.

[0023] First, for the control approach of a lattice constant, the average valence of the manganese ion which exists during a crystal is controlled paying attention to a lattice constant being dependent on the ionic radius of manganese.

[0024] First, there is the approach of controlling the ambient atmosphere at the time of composition, and controlling the average valence of manganese. For example, it is possible to control the average valence of manganese by filling up the interior of a firing furnace with the gas which mixed simple substances, such as gases, such as oxygen from which oxidizing power differs, atmospheric air and hydrogen, a carbon monoxide, and a carbon dioxide, inactive nitrogen, and an argon, or those some by the suitable ratio. Especially, it is desirable in manufacturing cost to use the simple substance of oxygen and the mixture of gas of oxygen and atmospheric air.

[0025] Moreover, there is also the approach of controlling the average valence of manganese by changing burning temperature. For example, when it calcinates in atmospheric air, at low temperature, the average valence of manganese is comparatively large, and the average valence of manganese is comparatively small at an elevated temperature conversely. However, if the discharge capacity of the manganic acid ghost from which crystallinity was bad acquired as it is low temperature too much becomes small and temperature is too high, in order to start a phase transition, 500 degrees C or more 1000 degrees C or less are desirable. It is more desirable to calcinate especially at 700-degree-C or more temperature of 1000 degrees C or less in respect of capacity.

[0026] Furthermore, the strong compound of oxidizing power and the strong compound of reducing power are used for the lithium compound and manganese compound used as a raw material, and there is also a method of mixing these by the suitable ratio. If manganese acetate is used for a raw material as an example, manganese will be returned, an average valence becomes small, a lattice constant becomes large, the manganese which uses manganese nitrate for a raw material conversely oxidizes, an average valence becomes large, and a lattice constant becomes small.

[0027] In addition, there is the approach of controlling the average valence of manganese etc. by replacing some manganese by other elements. Although a lithium, magnesium, aluminum, chromium, iron, nickel, cobalt, etc. are mentioned as an element which replaces some manganese, of course, you may be elements other than this.

[0028] furthermore, manganese -- superfluous -- carrying out -- the lithium in oxide, and the ratio of manganese -- it is also effective to make Li/Mn or less into 0.5.

[0029] Furthermore, there is also the approach of replacing a part of oxygen which is an anion with other anions with which valences differ. As an anion which replaces oxygen, although fluorine ion, nitrogen ion, etc. are mentioned, for example, it is not limited to these. However, in respect of a rate property, fluorine ion is desirable.

[0030] The approach mentioned above may be independently performed in control of a lattice constant, or some may be combined with it of them, and a lattice constant may be controlled.

[0031] Moreover, intensity ratio  $R=I(400)/I(311)$  of an X diffraction line expressed in (311) as a characteristic (400) is dependent on a presentation and gestalt of raw materials,



such as a lithium and manganese. Moreover, it is dependent also on a synthetic approach. Furthermore, it is dependent also on synthetic conditions, such as heating temperature, the persistence time of heating, a cooling rate, and an ambient atmosphere at the time of heating. For example, it sets in the example of this invention mentioned later. After heating to the temperature beyond 600 degrees C thru/or it, quench to a room temperature, and intensity ratio  $R=I(400)/I(311)$  is controlled by the approach of reheating it among atmospheric air for 5 hours or more with a certain 800-degree-C or more constant temperature of less than 900 degrees C among 700-degree-C or more less than 780 degrees C or an oxygen air current. The value of beta of (a formula 1) was made or less [ 7 or more ] into ten still more desirably 12 or less [ 6 or more ]. Moreover, for example, after heating with a certain constant temperature of less than 500 degrees C in the example of this invention mentioned later for 2 hours or more, and heating with the existing constant temperature of 700 degrees C or more for 5 hours or more, by cooling over 30 hours or more to 500 degrees C, intensity ratio  $R=I(400)/I(311)$  was controlled and the value of beta of an equation 1 was made or less [ 7 or more ] into ten still more desirably 12 or less [ 6 or more ].

[0032] Although the approach of the control of a lattice constant and intensity ratio  $R=I(400)/I(311)$  to the above was described, the control approach of a lattice constant and an intensity ratio is not what not necessarily became independent after this so that clearly. For example, the temperature of heating and an ambient atmosphere affect a lattice constant and an intensity ratio, and are said of the presentation of synthetic powder, for example. [ of the same ] Therefore, it is required to combine the approach for which it was suitable in order to control the value of beta of the degree type 1 or less [ 7 or more ] to ten still more desirably 12 or less [ 6 or more ] rather than to combine at random the approach described above.

(Configuration of a positive electrode) The positive electrode of this nonaqueous electrolyte cell mixes said positive-electrode ingredient, electric conduction material, and a binder, and is created by being stuck to a charge collector by pressure. Or a suitable solvent is made to suspend said positive-electrode ingredient, electric conduction material, and a binder, and you may create by applying this suspended solid to a charge collector, and drying.

[0033] As said electric conduction agent, acetylene black, carbon black, a graphite, etc. can be mentioned, for example.

[0034] As said binder, polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), an ethylene-propylene-diene copolymer (EPDM), a styrene butadiene rubber (SBR), etc. can be used, for example.

[0035] the blending ratio of coal of said positive-electrode ingredient, electric conduction material, and a binder -- 80 - 95 % of the weight of positive-electrode ingredients, and electric conduction material -- it is desirable to make it the range of 2 - 7 % of the weight of binders three to 20% of the weight. As said charge collector, the conductive substrate of the vesicular structure of aluminum, stainless steel, nickel, etc. or a nonporous conductive substrate can be used, for example.

(Separator) As said separator, the nonwoven fabric made of synthetic resin, a polyethylene porosity film, a polypropylene porosity film, etc. can be used, for example.

(Negative electrode) A lithium metal can be used as a negative-electrode ingredient of a negative electrode.

[0036] Moreover, as a negative-electrode ingredient, the carbon material other than a lithium metal in which a dope and a dedope are possible is mentioned [ lithium ] including a lithium metal in the alloy and metallic oxide in which a dope and a dedope are possible, metallic sulfide, a metal nitride, a chalcogen compound, and a lithium. Especially the negative electrode containing the carbon material or chalcogen compound in which a dope and a dedope of a lithium are possible has high safety, and since a cycle life is also high, it is desirable.

[0037] Since corks, a carbon fiber, a pyrolysis gaseous-phase carbon object, a graphite, a resin baking object, a mesophase pitch based carbon fiber, or mesophase pitch spherical carbon becomes [ electrode capacitance ] high considering said lithium ion as occlusion and a carbon material to emit, for example, it is desirable.

[0038] As a chalcogen compound in which a dope and a dedope of said lithium are possible, 2 titanium sulfides, molybdenum disulfide, selenium-ized niobium, the tin oxide, etc. can be mentioned. If such a chalcogen compound is used for a negative electrode, although it falls, since the capacity of said negative electrode increases, the capacity of cell voltage of said rechargeable battery will improve.

[0039] A negative electrode can knead said negative-electrode ingredient and binder under existence of a solvent, and can apply the obtained suspended solid to a charge collector, and the dry thing can be used for it.

[0040] In this case, as a binder, polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), an ethylene-propylene-diene copolymer (EPDM), a styrene butadiene rubber (SBR), etc. can be used, for example. Furthermore, as for the blending ratio of coal of said negative-electrode ingredient, electric conduction material, and a binder, it is desirable to make it the range of 90 - 98 % of the weight of negative-electrode ingredients and 2 - 10 % of the weight of binders. Moreover, as said charge collector, conductive substrates, such as aluminum, stainless steel, and nickel, can be used, for example.

(Nonaqueous electrolyte) The polymer gel-like nonaqueous electrolyte containing said non-aqueous solvent and said electrolyte, the giant-molecule solid-state nonaqueous electrolyte which uses said electrolyte as a principal component, the inorganic solid-state nonaqueous electrolyte which has lithium ion conductivity are mentioned to the liquid nonaqueous electrolyte prepared when said nonaqueous electrolyte dissolves an electrolyte in a non-aqueous solvent, and polymeric materials.

[0041] As a non-aqueous solvent in said liquid nonaqueous electrolyte for example, annular carbonate and chain-like carbonate (for example, ethylene carbonate --) PUROI en carbonate, diethyl carbonate, dimethyl carbonate, Cyclic ether, such as methylethyl carbonate, and the chain-like ether For example, (1, 2-dimethoxyethane, 2-methyl tetrahydrofuran), etc., cyclic ester and chain-like ester (for example, gamma-butyrolactone and gamma-valerolactone --) Although independent thru/or 2-5 sorts of mixed solvents chosen from delta-valerolactone, methyl acetate, ethyl acetate, propyl acetate, isopropyl acetate, methyl propionate, pro BION acid ethyl, propionic-acid propyl, etc. can use It is not necessarily limited to these.

[0042] As an electrolyte contained in said nonaqueous electrolyte, lithium salt, such as lithium perchlorate ( $\text{LiClO}_4$ ), a 6 phosphorus-fluoride acid lithium ( $\text{LiPF}_6$ ), hoe lithium fluoride ( $\text{LiBF}_4$ ), a 6 fluoride arsenic lithium ( $\text{LiAsF}_6$ ), a trifluoro meta-sulfonic-acid lithium ( $\text{LiCF}_3\text{SO}_3$ ), and a bis-trifluoromethylsulfonyl imide lithium [ $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ ], is mentioned, for example. Although one sort or 2-3 sorts of lithium salt chosen from

now on can be used as this electrolyte, it is not limited to these.

[0043] As for the amount of dissolutions to said non-aqueous solvent of said electrolyte, it is desirable to carry out in 0.5-2.0 mols/l.

[0044] Moreover, as macromolecule gel nonaqueous electrolyte, it is said non-aqueous solvent and the thing which dissolved said electrolyte in polymeric materials and was made into gel, and the polymer of monomers, such as a polyacrylonitrile, polyacrylate, polyvinylidene fluoride (PVdF), and polyethylene oxide (PECO), or a copolymer with other monomers is mentioned as polymeric materials.

[0045] As macromolecule solid-state nonaqueous electrolyte, it dissolves in polymeric materials and said electrolyte is solidified. As polymeric materials, the polymer of monomers, such as the poly AKURURIRO nitril, polyvinylidene fluoride, and polyethylene oxide (PEO), or the copolymer of other monomers is mentioned. Moreover, the ceramic ingredient which contained the lithium as inorganic solid-state nonaqueous electrolyte is mentioned.  $\text{Li}_3\text{N}$  and  $\text{Li}_3\text{PO}_4\text{-Li}_2\text{S-SiS}_2$  glass etc. is mentioned especially.

[0046]

[Example] Hereafter, an example is shown and this invention is explained.

(Example 1) The positive-electrode ingredient was obtained by the following approaches. It mixed so that the mole ratio of a lithium, aluminum, and manganese might become 1.07:0.10:1.83:, into atmospheric air, at 250 degrees C, it heated for 20 hours and continued, and at 750 degrees C, it heated for 50 hours, and cooled over 30 hours to 500 degrees C after that, and, finally the lithium nitrate of a raw material, the aluminium nitrate, and the manganese dioxide were annealed to the room temperature. The taken-out sample is ground, further, among atmospheric air and after heating at 800 degrees C for 72 hours, it cools slowly to a room temperature, and it is a lithium manganic acid ghost ( $\text{Li}_{1+x}\text{Mn}_{2-x-y}(\text{O}, \text{A})_4$  was obtained.).

[0047] The X diffraction line of this lithium manganic acid ghost was measured. The Measuring condition of the X diffraction line in this invention is described. Cu-K alpha 1 (wavelength of 1.54056A) was used for X line source. It is tube voltage [ of 50kV ], tube voltage [ of 300mA ], 0.5 degree [ of divergent slits ], 0.5 degree [ of scattering slits ], and light-receiving slit 0.15mm, and the monochromator was used further. Measurement was a part for scan step 0.02degree and scan speed/of 4 degrees. In order to ask for the lattice constant of a lithium manganic acid ghost, it mixed with Si (lattice constant of 5.43088A) of lattice constant known, and this Si was made into the internal standard sample.

[0048] the ratio showing the lattice constant  $a_0$ , the characteristic (400), and the diffraction line intensity of (311) which belonged by cubic  $\text{Fd}\bar{3}\text{m}$  of said lithium manganic acid ghost of I (400) and I (311) -- beta which obtained  $R=I(400)/I(311)$  and substituted the above-mentioned lattice constants  $a_0$  and R for (the formula 1) was 7.30.

[0049] The nonaqueous electrolyte rechargeable battery shown in drawing 1 was created by using this lithium manganic acid ghost as a positive-electrode ingredient. The positive electrode, the negative electrode, the separator 4, and the thing shown below as nonaqueous electrolyte were used.

[0050] The positive electrode of said cell produced the positive-electrode ingredient layer 2 which mixed Teflon at 3% of the weight of a rate, and obtained 80 % of the weight of said positive-electrode ingredients, and the acetylene black which is electric conduction material as 17 % of the weight and a binder, was stuck to the positive-electrode charge

collector 3 which consists of a network made from stainless steel to which this was beforehand welded by the cell can 8 by pressure, and produced it.

[0051] The negative electrode of said cell stuck by pressure and produced the negative-electrode ingredient layer 5 which becomes the negative-electrode charge collector 6 which consists of a network made from nickel beforehand welded to the cell lid 7 from a lithium metal.

[0052] The liquefied nonaqueous electrolyte which ethyl methyl carbonate and ethylene carbonate were mixed [ nonaqueous electrolyte ] at a rate of 2:1, and dissolved LiPF<sub>6</sub> in this at a rate of one mol/l. as nonaqueous electrolyte of said cell was used.

[0053] After carrying out the laminating of the cell can 8, said positive electrode, said separator 4, said negative electrode, and the cell lid 7 in this sequence, respectively, said electrolytic solution was poured in and the gasket and the cylindrical nonaqueous electrolyte rechargeable battery shown in drawing 1 which it obturated in total and was mentioned above were assembled.

[0054] Thus, the charge and discharge of 3 cycles were first performed for the created cell at 20 degrees C, and capacity was checked. Next, the charge-and-discharge cycle trial in 60 degrees C was performed. That is, it is 30 cycle \*\*\*\*\* about a charge-and-discharge cycle under a 60-degree C environment. The charge-and-discharge conditions at that time are as follows. That is, after charging to 4.3V by 1 mA/cm<sup>2</sup>, the circuit was opened for 30 minutes and then it discharged to 3.5V by 1 mA/cm<sup>2</sup>, and the circuit was opened for 30 minutes after that, and this was made into 1 cycle. And the discharge capacity of 30 cycle eye which set discharge capacity of 1 cycle eye to 100 was measured. It indicates to Table 1 by making this into a capacity maintenance factor.

(Example 2) The positive-electrode ingredient was obtained by the following approaches. The lithium nitrate of a raw material, the cobalt nitrate, and the manganese dioxide were mixed so that the mole ratio of a lithium, cobalt, and manganese might be set to 1.06:0.11:1.84, and after heating [ for 20 hours ] and heating at 750 degrees C continuously by 250 degrees C in atmospheric air for 50 hours, it cooled slowly to the room temperature. The taken-out sample was ground, and further, it heated for 72 hours, cooled [ at 800 degrees C, ] over 30 hours among atmospheric air, to 500 degrees C after that, and, finally cooled slowly to the room temperature, and the lithium manganic acid ghost (Li<sub>1+x</sub>MyMn<sub>2-x-y4</sub> (O, A)) was obtained.

[0055] the ratio showing the lattice constant  $a_0$ , the characteristic (400), and the diffraction line intensity of (311) which measured the X diffraction line of this lithium manganic acid ghost, and belonged by that cubic Fd3m of I (400) and I (311) --  $R=I(400)/I(311)$  was obtained. beta which substituted the above-mentioned lattice constants  $a_0$  and R for (the formula 1) was 7.28.

[0056] When it removed having used this sample as the positive-electrode ingredient, others created the nonaqueous electrolyte rechargeable battery by the same approach as an example 1, and performed the charge-and-discharge cycle trial in 60 degrees C. It indicates to Table 1 by making a result into a capacity maintenance factor.

(Example 3) The positive-electrode ingredient was obtained by the following approaches. Weighing capacity of the lithium nitrate of a raw material, an aluminium nitrate, and the manganese nitrate was carried out so that the mole ratio of a lithium, aluminum, and manganese might be set to 0.98:0.21:1.81, and this was dissolved in water. When this water solution was heated with the electric furnace and having been amounted to 600

degrees C, it took out from the electric furnace and quenched. This was heated at 750 degrees C among atmospheric air for 10 hours, and the lithium manganic acid ghost ( $\text{Li}_{1+x}\text{MyMn}_{2-x-y}\text{O}_4$  (O, A)) was obtained.

[0057] the ratio showing the lattice constant  $a_0$ , the characteristic (400), and the diffraction line intensity of (311) which measured the X diffraction line of this lithium manganic acid ghost, and belonged by that cubic  $\text{Fd}\bar{3}\text{m}$  of I (400) and I (311) --  $R=I(400)/I(311)$  was obtained. beta which substituted the above-mentioned lattice constants  $a_0$  and R for (the formula 1) was 7.15.

[0058] When it removed having used this lithium manganic acid ghost as the positive-electrode ingredient, others created the nonaqueous electrolyte rechargeable battery by the same approach as an example 1, and performed the charge-and-discharge cycle trial in 60 degrees C. It indicates to Table 1 by making a result into a capacity maintenance factor.

(Example 4) The positive-electrode ingredient was obtained by the following approaches. The lithium hydroxide and the manganese dioxide were mixed so that the mole ratio of a lithium and manganese might be set to 0.98:2.02. After heating this at 750 degrees C for 20 hours by heating for 20 hours and continuing at 475 degrees C into atmospheric air and cooling over 50 hours to 500 more degrees C, it cooled slowly to the room temperature and the lithium manganic acid ghost ( $\text{Li}_{1+x}\text{MyMn}_{2-x-y}\text{O}_4$  (O, A)) was obtained.

[0059] the ratio showing the lattice constant  $a_0$ , the characteristic (400), and the diffraction line intensity of (311) which measured the X diffraction line of this lithium manganic acid ghost, and belonged by that cubic  $\text{Fd}\bar{3}\text{m}$  of I (400) and I (311) --  $R=I(400)/I(311)$  was obtained. beta which substituted the above-mentioned lattice constants  $a_0$  and R for (the formula 1) was 6.71.

[0060] When it removed having used this sample as the positive-electrode ingredient, others created the nonaqueous electrolyte rechargeable battery by the same approach as an example 1, and performed the charge-and-discharge cycle trial in 60 degrees C. It indicates to Table 1 by making a result into a capacity maintenance factor.

(Example 5) The positive-electrode ingredient was obtained by the following approaches. The lithium hydroxide and the manganese dioxide were mixed so that a lithium and manganese might serve as a mole ratio 0.98:2.02. After heating this at 750 degrees C for 20 hours by heating for 20 hours and continuing at 475 degrees C into atmospheric air and cooling over 50 hours to 500 more degrees C, it cooled slowly to the room temperature. After carrying out grinding mixing of this, in atmospheric air, it heated at 800 degrees C for 72 hours, and the lithium manganic acid ghost ( $\text{Li}_{1+x}\text{MyMn}_{2-x-y}\text{O}_4$  (O, A)) was obtained.

[0061] the ratio showing the lattice constant  $a_0$ , the characteristic (400), and the diffraction line intensity of (311) which measured the X diffraction line of this lithium manganic acid ghost, and belonged by that cubic  $\text{Fd}\bar{3}\text{m}$  of I (400) and I (311) --  $R=I(400)/I(311)$  was obtained. beta which substituted the above-mentioned lattice constants  $a_0$  and R for (the formula 1) was 6.64.

[0062] When it removed having used this lithium manganic acid ghost as the positive-electrode ingredient, others created the nonaqueous electrolyte rechargeable battery by the same approach as an example 1, and performed the charge-and-discharge cycle trial in 60 degrees C. It indicates to Table 1 by making a result into a capacity maintenance

factor.

(Example 6) The positive-electrode ingredient was obtained by the following approaches. Weighing capacity of the lithium nitrate of a raw material, an aluminium nitrate, and the manganese nitrate was carried out so that the mole ratio of a lithium, aluminum, and manganese might be set to 0.98:0.21:1.81, and this was dissolved in water 1. When this water solution was heated with the electric furnace and having been amounted to 600 degrees C, it quenched by taking out from an electric furnace. This was heated at 800 degrees C among the oxygen air current for 80 hours, and the lithium manganic acid ghost ( $\text{Li}_{1+x}\text{Mn}_{2-x-y}\text{O}_4$  (O, A)) was obtained.

[0063] the ratio showing the lattice constant  $a_0$ , the characteristic (400), and the diffraction line intensity of (311) which measured the X diffraction line of this lithium manganic acid ghost, and belonged by that cubic  $\text{Fd}\bar{3}\text{m}$  of I (400) and I (311) --  $R=I(400)/I(311)$  was obtained. beta which substituted the above-mentioned lattice constants  $a_0$  and R for (the formula 1) was 6.45.

[0064] When it removed having used this sample as the positive-electrode ingredient, others created the nonaqueous electrolyte rechargeable battery by the same approach as an example 1, and performed the charge-and-discharge cycle trial in 60 degrees C. It indicates to Table 1 by making a result into a capacity maintenance factor.

(Example 1 of a comparison) The positive-electrode ingredient was obtained by the following approaches. Weighing capacity of the lithium hydroxide of a raw material, a cobalt nitrate, and the manganese dioxide was carried out so that the mole ratio of a lithium, manganese, and aluminum might be set to 1.05:0.10:1.85, this mixture was heated at 750 degrees C among atmospheric air for 20 hours, and the lithium manganic acid ghost ( $\text{Li}_{1+x}\text{Mn}_{2-x-y}\text{O}_4$  (O, A)) was obtained.

[0065] the ratio showing the lattice constant  $a_0$ , the characteristic (400), and the diffraction line intensity of (311) which measured the X diffraction line of this lithium manganic acid ghost, and belonged by that cubic  $\text{Fd}\bar{3}\text{m}$  of I (400) and I (311) --  $R=I(400)/I(311)$  was obtained. beta which substituted the above-mentioned lattice constants  $a_0$  and R for (the formula 1) was 5.87.

[0066] When it removed having used this lithium manganic acid ghost as the positive-electrode ingredient, others created the nonaqueous electrolyte cell by the same approach as an example 1, and performed the charge-and-discharge cycle trial in 60 degrees C. It indicates to Table 1 by making a result into a capacity maintenance factor.

(Example 2 of a comparison) The positive-electrode ingredient was obtained by the following approaches. The pellet was created having applied [ mixed the lithium hydroxide and the manganese dioxide so that a lithium and manganese might serve as a mole ratio 0.98:2.02, and ] the load of 5tons per two 1cm subsequently. This was continuously heated [ for 5 hours ] and heated at 1000 degrees C by 475 degrees C in the oxygen air current for 20 hours, and temperature was lowered to 750 more degrees C, it heated for 12 hours, and the lithium manganic acid ghost ( $\text{Li}_{1+x}\text{Mn}_{2-x-y}\text{O}_4$  (O, A)) was obtained.

[0067] the ratio showing the lattice constant  $a_0$ , the characteristic (400), and the diffraction line intensity of (311) which measured the X diffraction line of this lithium manganic acid ghost, and belonged by that cubic  $\text{Fd}\bar{3}\text{m}$  of I (400) and I (311) --  $R=I(400)/I(311)$  was obtained. beta which substituted the above-mentioned lattice constants  $a_0$  and R for (the formula 1) was 4.99.

[0068] When it removed having used this sample as the positive-electrode ingredient, others created the nonaqueous electrolyte rechargeable battery by the same approach as an example 1, and performed the charge-and-discharge cycle trial in 60 degrees C. A result is indicated to Table 1.

(Example 3 of a comparison) The positive-electrode ingredient was obtained by the following approaches. As an example of a comparison, a lithium hydroxide and manganese carbonate were mixed so that a lithium and manganese might serve as a mole ratio 1.00:2.00, this mixture was heated at 475 degrees C among the oxygen air current for 5 hours, it heated at 750 more degrees C for 12 hours, and the lithium manganic acid ghost ( $\text{Li}_{1+x}\text{MyMn}_{2-x-y}\text{O}_4$  (O, A)) was obtained.

[0069] the ratio showing the lattice constant  $a_0$ , the characteristic (400), and the diffraction line intensity of (311) which measured the X diffraction line of this lithium manganic acid ghost, and belonged by that cubic  $\text{Fd}3\text{m}$  of I (400) and I (311) --  $R=I(400)/I(311)$  was obtained. beta which substituted the above-mentioned lattice constants  $a_0$  and R for (the formula 1) was 4.66.

[0070] When it removed having used this lithium manganic acid ghost as the positive-electrode ingredient, others created the nonaqueous electrolyte cell by the same approach as an example 1, and performed the charge-and-discharge cycle trial in 60 degrees C. It indicates to Table 1 by making a result into a capacity maintenance factor.

(Example 4 of a comparison) The following approach positive-electrode ingredients were obtained. Weighing capacity of the lithium nitrate of a raw material and the manganese acetate was carried out so that a lithium and manganese might serve as a mole ratio 1.02:1.98, and this was dissolved at a rate of 1.6 mols to 1l. of water. This water solution was sprayed on the interior of a 200-degree C furnace at a rate of 2.5kg/h. The obtained powder was heated at 800 degrees C among atmospheric air for 72 hours, and the lithium manganic acid ghost ( $\text{Li}_{1+x}\text{MyMn}_{2-x-y}\text{O}_4$  (O, A)) was obtained.

[0071] the ratio showing the lattice constant  $a_0$ , the characteristic (400), and the diffraction line intensity of (311) which measured the X diffraction line of this lithium manganic acid ghost, and belonged by that cubic  $\text{Fd}3\text{m}$  of I (400) and I (311) --  $R=I(400)/I(311)$  was obtained. beta which substituted the above-mentioned lattice constants  $a_0$  and R for (the formula 1) was 4.10.

[0072] When it removed having used this sample as the positive-electrode ingredient, others created the nonaqueous electrolyte cell by the same approach as an example 1, and performed the charge-and-discharge cycle trial in 60 degrees C. It indicates to Table 1 by making a result into a capacity maintenance factor.

(Example 5 of a comparison) The positive-electrode ingredient was obtained by the following approaches. The lithium hydroxide and the manganese dioxide were mixed so that a lithium and manganese might serve as a mole ratio 0.98:2.02, this was continuously heated [ for 5 hours ] and heated at 1000 degrees C by 475 degrees C in the oxygen air current for 20 hours with powder, and temperature was lowered to 750 more degrees C, it heated for 12 hours, and the lithium manganic acid ghost ( $\text{Li}_{1+x}\text{MyMn}_{2-x-y}\text{O}_4$  (O, A)) was obtained.

[0073] the ratio showing the lattice constant  $a_0$ , the characteristic (400), and the diffraction line intensity of (311) which measured the X diffraction line of this lithium manganic acid ghost, and belonged by that cubic  $\text{Fd}3\text{m}$  of I (400) and I (311) --  $R=I(400)/I(311)$  was obtained. beta which substituted the above-mentioned lattice

constants  $a_0$  and  $R$  for (the formula 1) was 2.95.

[0074] When it removed having used this sample as the positive-electrode ingredient, others created the nonaqueous electrolyte rechargeable battery by the same approach as an example 1, and performed the charge-and-discharge cycle trial in 60 degrees C. It indicates to Table 1 by making a result into a capacity maintenance factor.

(Example 6 of a comparison) The nonaqueous electrolyte cell was created by the same approach as an example 1 using the same positive-electrode ingredient as the example 3 of a comparison. In the charge-and-discharge cycle trial, in the example 1, temperature was changed and the charge-and-discharge cycle trial in 20 degrees C was performed. It indicates to Table 1 by making a result into a capacity maintenance factor.

[0075] The presentation ratio  $x$ ,  $y$  and  $z$ ,  $a_0$ ,  $R$  and  $\beta$ , the test temperature, capacity maintenance factor, and BET specific surface area of Li, M, and Mn of the lithium manganic acid ghost ( $\text{Li}_{1+x}\text{M}_y\text{Mn}_{2-x-y}\text{O}_4$  (O, A)) of each example and the example of a comparison are indicated.

[Table 1]

組成		$a_0$	$R$	$\beta$	試験温度	容量維持率	BET表面積	
		オクシド			°C	%	m <sup>2</sup> /g	
実施例	1	Li <sub>1.07</sub> Al <sub>0.10</sub> Mn <sub>1.83</sub> O <sub>4</sub>	8.207	1.12	7.30	60	92	3.16
実施例	2	Li <sub>1.06</sub> Co <sub>0.11</sub> Mn <sub>1.84</sub> O <sub>4</sub>	8.209	1.05	7.28	60	94	1.96
実施例	3	Li <sub>0.98</sub> Al <sub>0.21</sub> Mn <sub>1.81</sub> O <sub>4</sub>	8.202	1.15	7.15	60	87	8.36
実施例	4	Li <sub>0.98</sub> Mn <sub>2.02</sub> O <sub>4</sub>	8.222	1.04	6.71	60	83	4.74
実施例	5	Li <sub>0.98</sub> Mn <sub>2.02</sub> O <sub>4</sub>	8.226	1.11	6.64	60	82	5.60
実施例	6	Li <sub>0.98</sub> Al <sub>0.21</sub> Mn <sub>1.81</sub> O <sub>4</sub>	8.207	1.18	6.45	60	82	2.71
比較例	1	Li <sub>1.05</sub> Co <sub>0.10</sub> Mn <sub>1.85</sub> O <sub>4</sub>	8.210	0.96	5.87	60	74	2.10
比較例	2	Li <sub>0.98</sub> Mn <sub>2.02</sub> O <sub>4</sub>	8.232	1.21	4.99	60	72	0.46
比較例	3	Li <sub>1.00</sub> Mn <sub>2.00</sub> O <sub>4</sub>	8.242	0.95	4.66	60	69	3.94
比較例	4	Li <sub>1.02</sub> Mn <sub>1.98</sub> O <sub>4</sub>	8.245	0.93	4.10	60	60	0.70
比較例	5	Li <sub>0.98</sub> Mn <sub>2.02</sub> O <sub>4</sub>	8.228	0.88	2.95	60	65	0.33
比較例	6	Li <sub>1.00</sub> Mn <sub>2.00</sub> O <sub>4</sub>	8.242	0.95	4.66	20	87	3.94

In the case of an example 1 to the example 6 to which the beta value of (a formula 1) used six or more lithium manganic acid ghosts for the positive-electrode ingredient, it turns out that a cycle capacity fall at 60 degrees C is very small so that clearly from Table 1.

[0076] On the other hand, when the beta value of (a formula 1) uses less than six lithium manganic acid ghost for a positive-electrode ingredient, it turns out that a cycle capacity fall at 60 degrees C is very large as shown in the example 5 of a comparison from the example 1 of a comparison.

[0077] In the example 3 of a comparison, and the example 6 of a comparison, the same lithium manganic acid ghost is used for a positive-electrode ingredient, and the case where a charge-and-discharge cycle is repeated at 60 degrees C and 20 degrees C, respectively is shown. Since the beta value of (a formula 1) is less than six, said lithium manganic acid ghost has a remarkable cycle capacity fall at 60 degrees C at 20 degrees C, even if a cycle capacity fall is small. This shows that the lithium manganic acid ghost whose beta value of (a formula 1) is less than six is very weak to a temperature rise from a viewpoint of cycle capacity maintenance. It exchanges for it and the lithium manganic acid ghost of an example 1 to the example 6 which experimented at 60 degrees C shows the case of the example 5 of a comparison performed at 20 degrees C, and the engine performance more than an EQC, the temperature dependence of a cycle capacity fall is very small, and maintaining the engine performance excellent also in the elevated



temperature is shown.

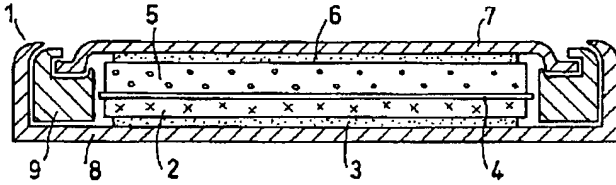
[0078] Moreover, in an example 1 - the example 6, to that to which specific surface area exceeds about  $2\text{m}^2/\text{g}$  to  $8\text{m}^2/\text{g}$ , regardless of specific surface area, even if it repeats charge and discharge at 60 degrees C, it turns out that it is possible to suppress the fall of capacity very low.

[0079]

[Effect of the Invention] As explained above, even if it repeats charge and discharge under the temperature exceeding the room temperature which is practical operating temperature limits, the nonaqueous electrolyte rechargeable battery which used the lithium manganic acid ghost with little reduction in capacity for the positive-electrode ingredient can be obtained.

[0080] Moreover, since it does not depend on the specific surface area but the above-mentioned effectiveness is acquired, the lithium manganic acid ghost of this invention can offer the suitable nonaqueous electrolyte rechargeable battery for the application which needs the rechargeable battery which was excellent in the high current property, therefore was excellent in the high current property, for example, an electric vehicle etc.

[0081] Furthermore, in order to use cheap manganese for a raw material, the manufacturing cost of a cell is pressed down low, and therefore, this cell can offer a cheap nonaqueous electrolyte rechargeable battery.



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